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Biological Removal of Manganese and Iron in Rapid Sand Filters

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Introduction

In Denmark and many other European countries, drinking water is exclusively or mainly based on groundwater. Treatment of the groundwater is rather simple, only including aeration and a subsequent filtration process. The filtration process may take place over two steps. Step 1: Filtration in a pre-filter, where iron is removed. Step 2: Filtration in an after-filter where e.g. ammonium and manganese is removed. The treatment relies on microbial processes and may present an alternative, greener and more sustainable approach for drinking water production spending less chemicals and energy than chemical (e.g. flocculation) and physical (e.g. membrane filtration) based technologies.

The removal of dissolved manganese and iron is important. If manganese and iron enter the distribution system, the water will become coloured and have a metallic taste, and it may cause problems in the distribution network due to precipitation and corrosion.

Manganese and iron can either be removed physico-chemically or biologically or combined. The physico-chemical oxidation and precipitation of manganese can theoretically be achieved by aeration, but this process is slow unless pH is raised far above neutral, making the removal of manganese by simple aeration and precipitation under normal drinking water treatment conditions insignificant. Manganese may also adsorb to the existing filter material, which may result in an autocatalytic oxidation of manganese. Iron is usually easier to remove. First, iron is rapidly chemically oxidized by oxygen at neutral pH followed by precipitation and filtration. For many years, research has focused on the biological removal of manganese and iron, due to the associated energy and chemical savings (Burger et al., 2008; Katsoyiannis and Zouboulis, 2004; Mouchet, 1992; Tekerlekopoulou et al., 2008; Vandenabeele et al., 1992). Furthermore, biological oxidation of manganese and iron results in denser precipitates than those obtained by chemical oxidation, reducing the number of required backwashes due to clogging of the filters.

The start-up of new filters is often based on “rules of thumb” procedures. New filters are often inoculated with sand from existing filters or backwash sludge, but this results in unpredictable start-up of filter performances. To obtain a well-functioning filter with biological manganese or iron removal, it is essential to ensure that the required microorganisms are present and that both the physical and the nutritional requirements of those organisms are fulfilled. However, the knowledge on the microbiology and processes in rapid sand filters is limited, especially on which parameters affect the biological processes and the interaction between them. Some studies have indicated a direct competition between iron and ammonium removal when oxygen is

limited, and both processes may have a negative effect on the manganese removal (de Vet et al., 2009; Tekerlekopoulou et al., 2008). However the reasons for these effects remain unclear.

The aim of this study was to develop a batch assay to quantify microbial manganese and iron removal and to investigate the effect of interactions between the ammonium, manganese and iron removal processes. The study is an on-going investigation and represents preliminary results and conclusions and is a part of the project “DWBiofilters – Sustainable drinking water treatment, biological filters” (Albrechtsen et al., 2012).

Manganese and iron removal assay - Experimental approach

An assay was developed to quantify microbial manganese and iron removal. It was based on short time incubation of filter material taken from operating water works (Islevbro water works, Rødovre, Denmark), where manganese and iron removal was followed over time. The filter material was gently washed with 1L treated water per 100 g (wet weight) of filter material in a sieve to get rid of unbound iron precipitates. To start the assay 10 g (wet weight) of filter material from an after filter was incubated with 400 mL water from the same water works (in a 500 mL infusion bottle (closed system)), where ammonium, manganese(II) and/or iron(II) were added and where the oxidation and adsorption was determined frequently over time (Figure 1). Samples (10 mL) over time was taken out by a syringe and acidified immediately to a pH below 2 with HCl.

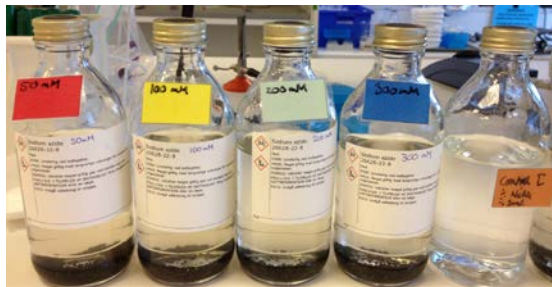


Figure 1: Experimental setup. 10 g filter material (from an after-filter) was incubated with 400 mL treated water in a 500 mL bottle. Ammonium, manganese(II) and/or iron(II) was added and concentrations followed over time. Bottles were incubated in an incubator with orbital shaking at 140 rpm at 10°C.

The oxygen concentration was at 10 mg/L or 5 mg/L and pH was at 7.5 or 6.5. Oxygen concentration of 10 mg/L and pH of 7.5 reflect the actual conditions in the test water. In order to adjust the conditions to a lower pH and oxygen concentration, the test water was flushed with 80% N₂/20% CO₂ until oxygen concentration was close to zero and the pH was 6.5. Pure oxygen was then added to a final concentration of 5 mg/L. To distinguish between biological and non-biological removal, control experiments were established by incubating the filter material with, sodium azide, a general poison (0.1 M, 24 hours) prior to the experiment and then removed before the start of the assay. Filter material treated with sodium azide were hereafter called “abiotic”.

All experiments were conducted at realistically low manganese, iron and ammonium concentrations and temperature (10°C) resembling conditions in Danish rapid sand filters (Table 1).

Table 1: Water quality and guidelines. Raw water and treated water quality of selected chemical species at Islevbro water works and Danish guideline values.

Chemical species	Raw water [mg/L]	Treated water [mg/L]	Guideline [mg/L]
NH_4^+	~ 0.5	<0.01	0.05
Fe^{2+}	~ 2	<0.005	0.1
Mn^{2+}	<0.5	<0.005	0.02
O_2	<0.4	10	5

All batches were shaken on an orbital shaker at 140 rpm to ensure proper mixing to eliminate mass transfer limitations. Total iron and manganese were measured by ICP-MS whereas Fe(II) was measured with the Ferrozine method (Stookey, 1970).

Results

Manganese removal and the effect of iron and ammonium

Manganese removal and the effect of iron and ammonium were first investigated with filter material retrieved from different filter depths. The manganese removal rate was highest in the top of the filter and decreased with filter depth (Figure 2). The abiotic controls, treated with sodium azide, showed a slightly lower removal rate, indicating contribution of biological reactions to the manganese removal in the filters.

Ammonium at a given concentration had a positive effect on manganese removal (Figure 3). Previous studies show cases of both negative and positive effect of nitrification on manganese removal (Vandenabeele et al., 1995; 1992). Iron had a negative effect on manganese removal and in some cases even caused an increase of manganese (Figure 4). This effect has been observed in other studies (Tekerekopoulou et al., 2008), and may be caused by the oxidation of Fe(II) by Manganese oxides (such as MnO_2) which are then reduced to Mn(II) (Postma and Appelo, 2000). No interaction effect between iron and ammonium on manganese removal was observed (data not shown).

Inhibition of microbial activity

In order to further verify the difference between biotic and abiotic removal rates, different methods to inactivate microbial activity were tested. Concentrations of sodium azide ranging from 50 mM to 2 M were tested. Furthermore, one and two hours of heating at 70°C or autoclaving at 120°C for 20 minutes were tested. Surprisingly, the results indicated that there was no difference between biotic and abiotic manganese removal rates and all abiotic removal rates were similar (Figure 5), questioning the presence of biological manganese removal or the experimental procedure.

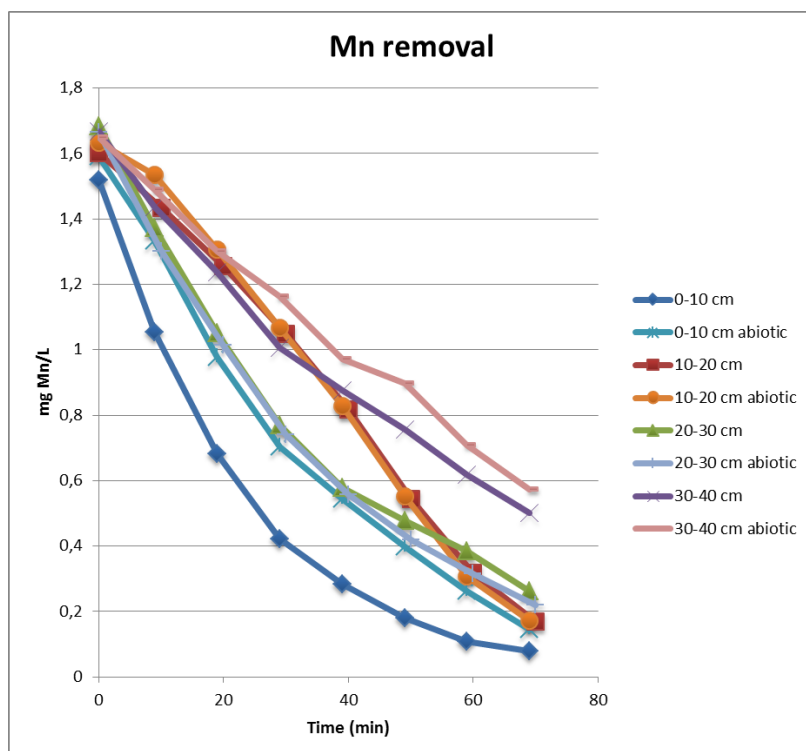


Figure 2: Manganese removal. 10 g of filter material from different depths of the full scale after-filter (Islebro water works) was incubated with 400 mL treated water and manganese(II) was added to a final concentration of approximately 1.6 mg/L. Abiotic filter material was treated with 0.1 M sodium azide for 24 hours prior to the experiment. Oxygen concentration: 10 mg/L, pH: 7.5. Manganese concentrations over time were measured by ICP-MS.

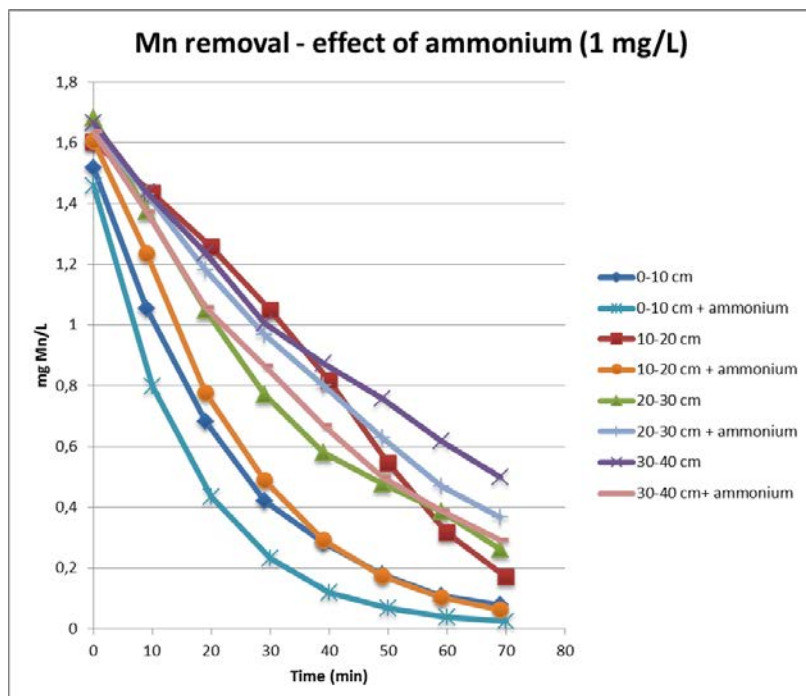


Figure 3: Manganese removal - The effect of ammonium. 10 g of filter material from different depths of the full scale after-filter (Islebro water works) was incubated with 400 mL treated water and manganese(II) and ammonium was added to a final concentration of approximately 1.6 mg/L and 1 mg/L respectively. Oxygen concentration: 10 mg/L, pH: 7.5. Manganese concentrations over time were measured by ICP-MS.

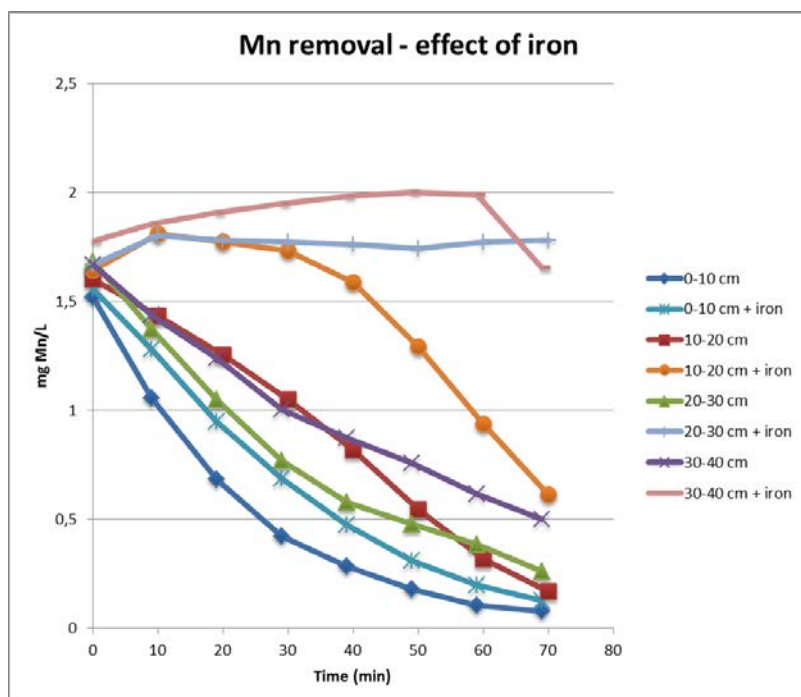


Figure 4: Manganese removal - The effect of iron. 10 g of filter material from different depths of the full scale after-filter (Islebro water works) was incubated with 400 mL treated water and manganese(II) and iron(II) was added to a final concentration of approximately 1.6 mg/L and 2 mg/L respectively. Oxygen concentration: 10 mg/L, pH: 7.5. Manganese and iron concentrations over time were measured by ICP-MS.

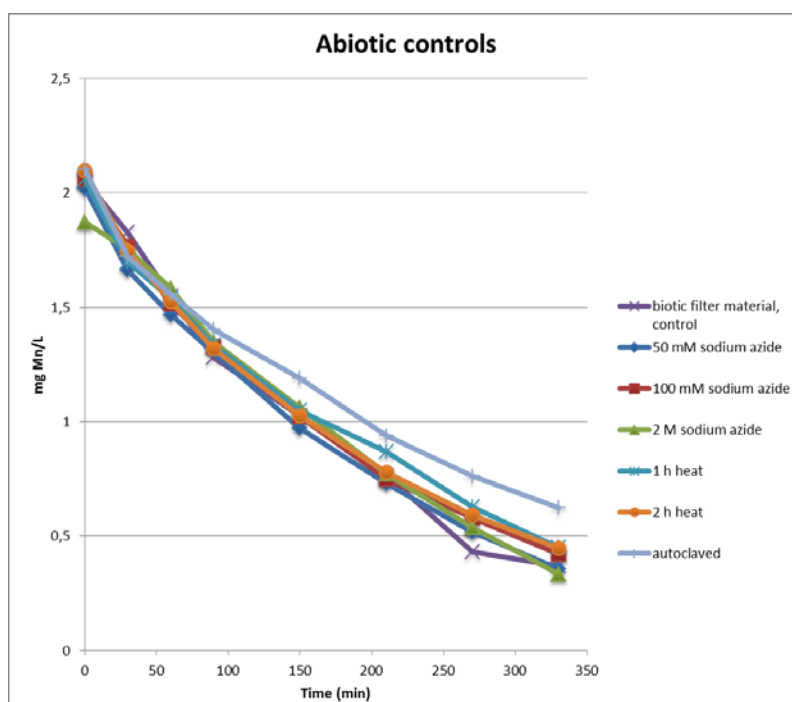


Figure 5: Abiotic controls. 10 g of filter material of the full scale after-filter (Islebro water works) was incubated with 400 mL treated water and manganese(II) was added to a final concentration of approximately 2 mg/L. Oxygen concentration: 10 mg/L, pH: 7.5. Abiotic filter material was treated in different ways to inhibit microbial activity: incubation with 50 mM, 100 mM or 2 M sodium azide for 24 hours, heating at 70°C for 1 or 2 hours or autoclaved at 120°C for 20 minutes. Manganese concentrations over time were measured by ICP-MS.

To test the experimental setup as well as investigate biological iron removal, sand from a pre-filter from Astrup water works (Esbjerg, Denmark) specifically designed to remove iron biologically was investigated. However these results also did not show any difference in biotic and abiotic filter material (data not shown), further questioning the experimental setup.

Investigation of iron(II) removal

Previously all samples during a batch time course were collected by a syringe, passed through a 0.2 μm filter, acidified and analysed for total iron and manganese in the filtrate. It was assumed that the main remaining manganese and iron species would be dissolved (II) and Fe(II). It is generally believed that chemical and/or biological oxidation is the main processes removing manganese and iron, whereas adsorption is a secondary removal process. In full-scale filters occupation of adsorption sites would result in a rapid decrease in filter performance. However, in view of our earlier experimental observations, we tested a new hypothesis which included the significance of adsorption of Fe(II) alone or in combination with biological and chemical oxidation in the batch assays on Fe(II) removal. This was tested by analysing Fe(II) in the water phase over time and analysed together with the amount of adsorbed Fe(II) in the filter material in order to be able to quantify the amount of oxidized vs. adsorbed iron. This was conducted with a similar experimental setup as above but with different lengths of incubation time with Fe(II). Furthermore, the significance of chemical vs. biological iron oxidation were determined by creating conditions that favoured chemical (O_2 concentration of 10 mg/L and pH 7.5) over biological iron oxidation (oxygen (5 mg O_2 /L) and pH level (pH 6.5)) (Mouchet, 1992). At the end of incubation, the water phase was discarded and the filter material extracted by 0.5 M HCl for one hour to dissolve bound Fe(II). The extractions were done in triplicates. The extract was filtered and analysed for Fe(II). This experiment was carried out with filter material from an after-filter at Islevbro water works. The results show that under reference conditions the filter material removes Fe(II) slightly faster than under biologically inhibited (NaN_3 spiked) conditions (Figure 6). These results indicate that biological iron oxidation may take place across a larger range of pH and oxygen conditions than described in the literature. The results also show that Fe(II) is removed faster in the presence of filter material. Furthermore, there was a general tendency of higher removal rates at high level of oxygen and at pH slightly above neutral. Thus the presence of filter material, oxygen level and pH has a large effect on the Fe(II) removal. More Fe(II) was extracted from the sodium azide treated than from the untreated filter material (Figure 7). This type of experiment has not been done before and the surprising results suggest that microbial Fe(II) oxidizing activity, which would convert Fe(II) to Fe(III), reduces the amount of surface adsorbed Fe(II). These results are preliminary, and further experiments are needed to verify this hypothesis.

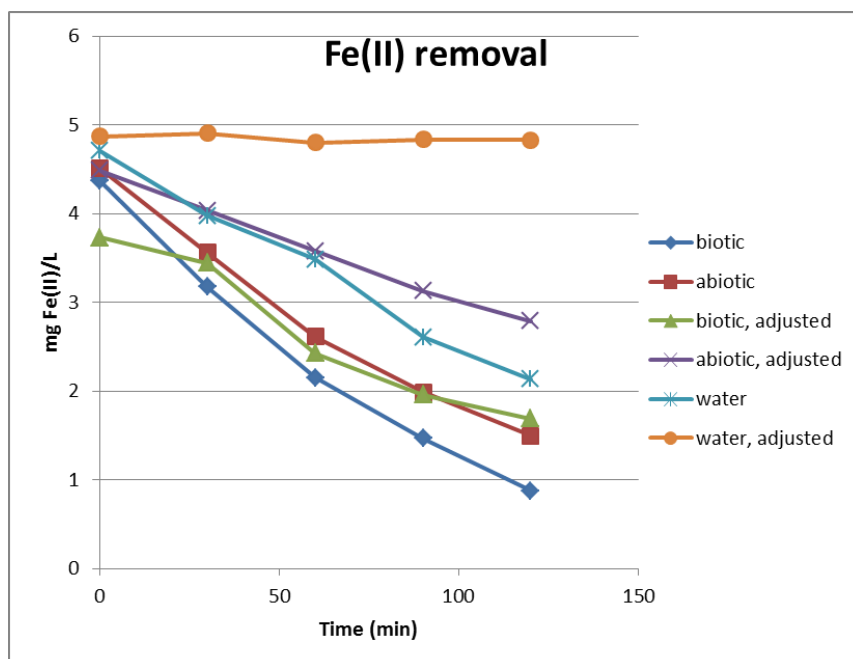


Figure 6: Iron(II) removal. 10 g of filter material of the full scale after-filter (Islevbro water works) was incubated with 400 mL treated water and iron(II) was added to a final concentration of approximately 5 mg/L. Oxygen concentration 10 mg/L and pH 7.5 or adjusted to oxygen concentration of 5 mg/L and pH 6.5. Abiotic filtermaterial was incubated with 0.1 M sodium azide for 24 hours prior to the experiment. Iron(II) concentrations over time were measured by the ferrozine method (Stookey, 1970).

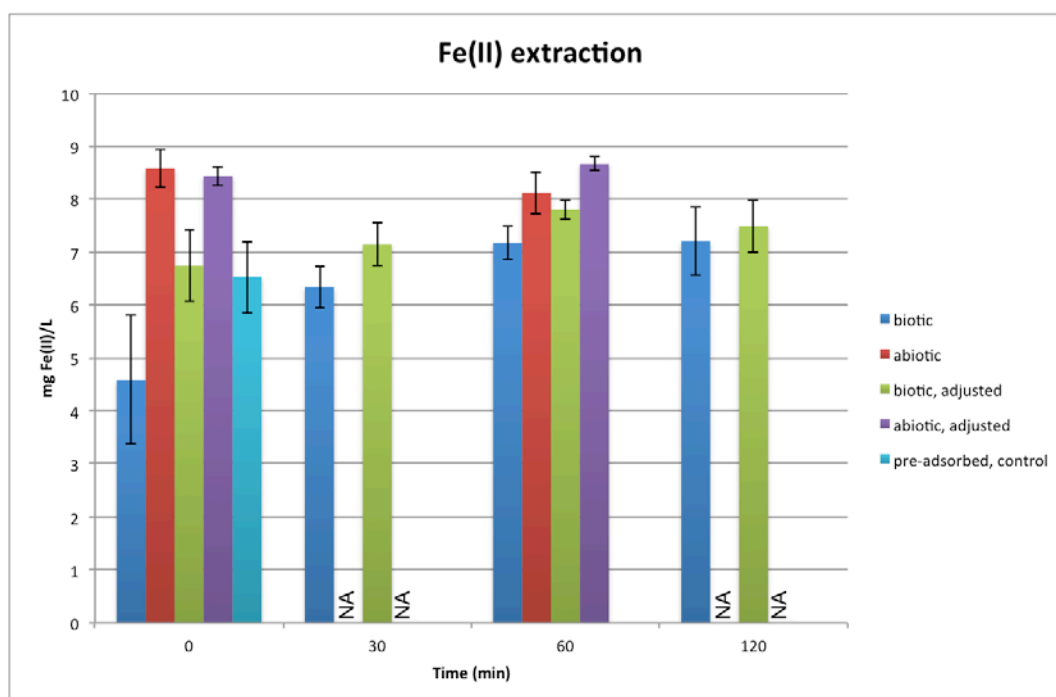


Figure 7: Fe(II) extractions. 10 g of filter material of the full scale after-filter (Islevbro water works) were incubated with 400 mL treated water and iron(II) was added to a final concentration of approximately 5 mg/L. Regular conditions: DO 10 mg/L and pH 7.5 or adjusted conditions: DO 5 mg/L and pH 6.5. After 0, 30, 60 and 120 minutes, the water was discarded and the filter material extracted in 0.5 M HCl for 1 hour to dissolve bound Fe(II). The pre adsorbed control represents the amount of adsorbed Fe(II) to the filter material prior to addition of 5 mg Fe(II)/L. Abiotic conditions were created by incubating filter material with 0.1 M sodium azide for 24 hours prior to the experiment. Iron(II) concentrations were measured by the ferrozine method (Stookey, 1970). NA: Not available data

Conclusion

A batch assay was developed to quantify the microbial manganese and iron removal. The assay allows testing the effect of various parameters as well as distinguishing between biological and non-biological removal processes.

The general tendency through the depth of a filter was that the manganese removal rate was highest in the top of the filter and decreased throughout the depth. Biological manganese removal could be detected, but the non-biological removal had a large role in removal performance as well.

The interaction between nitrification, manganese and iron removal was investigated and showed that ammonium had a positive effect on manganese removal whereas iron had a negative effect on manganese removal and even caused an increase of manganese.

Investigation of biological iron removal may require that Fe(II) is measured in the water phase as well as the adsorbed Fe(II) on the surface on the filter material in order to detect biological iron removal. The results showed that biological iron removal was present and increased the iron removal rate and that pH and oxygen level are important parameters. Surprisingly biological iron oxidation takes place at higher pH and oxygen level than previously observed. When filter material was not treated with sodium azide, less Fe(II) was adsorbed to the surface of the filter material, indicating that iron oxidizing bacteria contribute to the conversion of Fe(II) to Fe(III).

These conclusions are based on preliminary results. Further studies will aim at verifying the preliminary results and identify the most important controlling parameters on biological manganese and iron removal and their effect.

Acknowledgement

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